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Abstract: Geological mapping east of James Bay has revealed abundant, newly recognized north- to northwest- and northeast-trending Proterozoic diabase dykes in a part of the eastern Superior Province where information was previously scant. A magmatic crystallization age of 2069 ± 1 Ma (U-Pb, baddeleyite) was reported for a representative of the north- to northwest-trending Lac Esprit swarm, distinguishing it from similar-trending but older Matachewan and Mistassini dykes of the region. The Lac Esprit dykes represent an extensive diabase swarm with a Paleoproterozoic age so far unrecognized elsewhere in the eastern Superior Province. The age, together with published preliminary paleomagnetic results, invites comparisons with a postulated, regionally extensive, radiating swarm north of Lake Superior (Fort Frances and reversely magnetized Marathon dykes), among others. The new dyke age contributes information to dyke swarm correlations in the Superior Craton and also aids in the assessment of models promoting apparent polar wander and continental drift of Laurentia during the Paleoproterozoic, or block rotation since this time.

Résumé : Dans un secteur de la partie orientale de la Province du lac Supérieur où on avait jusqu'ici peu de données, des travaux de cartographie géologique menés à l'est de la baie James ont permis d'identifier de nombreux dykes de diabase du Protérozoïque appartenant à un ensemble reconnu depuis peu et qui affichent des directions nord à nord-ouest et nord-est. On a déterminé à 2 069 ± 1 Ma l'âge de la cristallisation magmatique (U-Pb sur baddeleyite) d'un échantillon représentatif de l'essaim de dykes de direction nord à nord-ouest du lac Esprit; cette datation permet de distinguer ces dykes de ceux des essaims de Matachewan et de Mistassini qui sont aussi représentés dans la région par des dykes d'orientation semblable, mais plus anciens. Les dykes du lac Esprit appartiennent à un vaste essaim de dykes de diabase du Paléoprotérozoïque qui définissent une classe chronologique dont on n'a pas reconnu jusqu'à présent de représentants ailleurs dans l'est de la Province du lac Supérieur. L'âge, ainsi que les résultats publiés d'études paléomagnétiques préliminaires nous amènent à établir des comparaisons avec d'autres grands ensembles, dont un vaste essaim de dykes à configuration radiale d'importance régionale situé au nord du lac Supérieur (les dykes de Fort Frances et les dykes de Marathon à polarité magnétique inverse). L'âge nouvellement attribué à ces dykes ajoute un élément d'information aux études de corrélation des essaims de dykes du craton du lac Supérieur. Il permet aussi d'évaluer deux modèles tectoniques qui proposent soit une migration apparente des pôles et une dérive continentale de la Laurentie au cours du Paléoprotérozoïque, soit une rotation en bloc depuis cette période.

INTRODUCTION

Recent geological mapping in the east-central Superior Province, led by the ministère des Ressources naturelles du Québec, has focused on Neoarchean rocks of the Bienville and La Grande subprovinces in the Yasinski Lake area, due east of James Bay (Fig. 1; Goutier et al., 1998a, b, 1999). South of the Robert Bourassa Reservoir, rocks of La Grande Subprovince comprise tonalitic gneiss, volcanosedimentary units, abundant tonalite and granite, and lesser ultramafic and gabbroic bodies. Uranium-lead geochronological studies in the area have revealed a complex geological evolution spanning at least 2794–2618 Ma (Goutier et al., 1998b, 1999; Mortensen and Ciesielski, 1987).

The Archean rocks of the entire Yasinski Lake region are now recognized as being transected by extensive swarms of undeformed and unmetamorphosed north-, northwest-, and northeast-trending diabase dykes (Goutier et al., 1998b, 1999). This represents a new and regionally significant set of dykes in the eastern Superior Province in an area where previous information about diabase dyke swarms was sparse. Dykes in the region vary in thickness up to approximately 100 m, generally form positive topographic relief, and frequently manifest themselves as strong, semicontinuous linear features on aeromagnetic survey maps because of their strong magnetic susceptibility. A preliminary study of a northeast-trending dyke that cuts the Amisach Wat Pluton northeast of Yasinski Lake revealed paleomagnetic directions suggesting clearly that the regional dykes of this trend belong to the well characterized northeast-striking Paleoproterozoic (2216 +8/-4 Ma) Senneterre swarm (Buchan et al., 1996; Ernst et al., 1998).

The north- to northwest-trending diabase dykes in the Yasinski Lake area east of James Bay are characterized by their orientation, grey to dark green colour, and brown weathering, the last of which sets them apart from other, hornblende-bearing metagabbro dykes. The dykes are commonly subophitic, and locally glomeroporphyritic, with plagioclase phenocrysts (typically saussuritized) up to 2 cm in length. These have been informally named the Lac Esprit dyke swarm (Goutier et al., 1999). Dykes of this orientation closely parallel the strike of regionally extensive swarms of earliest Paleoproterozoic north- to northwest-trending Matachewan dykes (ca. 2473–2446 Ma), as well as northwest-trending Mistassini dykes (ca. 2475 Ma), which have been described to the southwest and southeast of the field area, respectively (Heaman, 1997; Ernst et al., 1996). However, paleomagnetic poles from the north- to northwest-trending dykes of the study area are usually very different from those obtained from earliest Paleoproterozoic swarms of the Superior Province, such as the Matachewan (Ernst et al. 1998). Only a single dyke

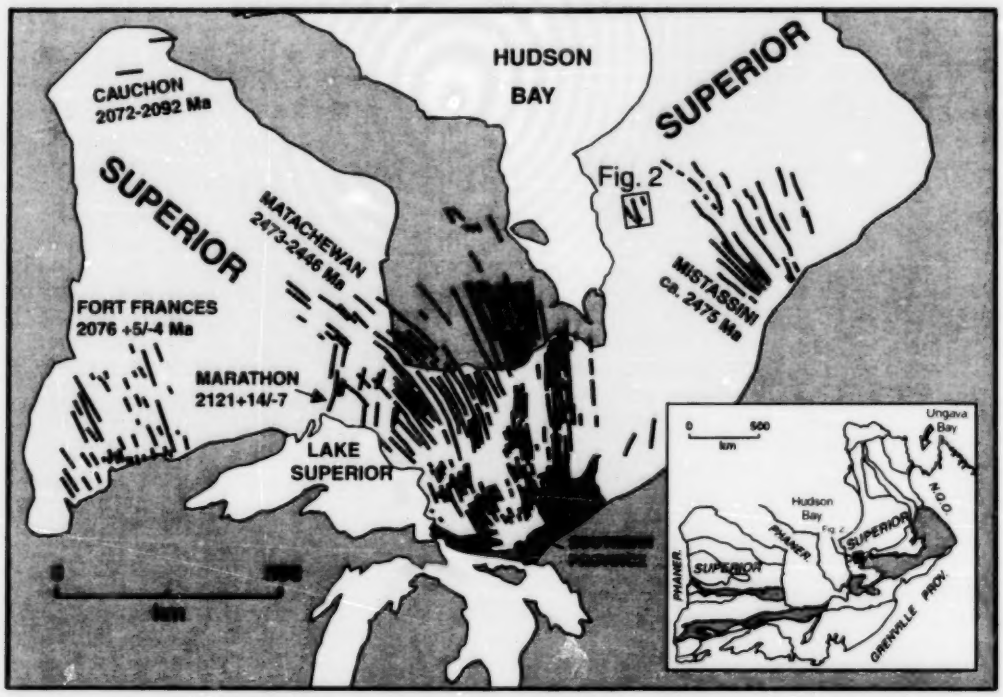

Figure 1. *Regional map showing the location of the Lac Esprit dykes (outlined box) relative to the position of the Matachewan, Mistassini, Fort Frances, Marathon and Cauchon Lake–Birthday Rapids dyke swarms. U-Pb ages are indicated.* See *text for sources. Inset shows the map boundaries (thin lines) of the Superior Province; metasedimentary terranes are shown shaded. N.Q.O.– New Quebec Orogen, Phaner.– Phanerozoic cover.*

carries a paleopole similar to the Matachewan pole. On the other hand, the paleopoles for most north- to northwest-trending dykes in the area fall close to, but are statistically distinct from, paleopoles for 2121–1998 Ma dykes in the Superior Province. These include the north-trending 2121 +14/-7 Ma normally magnetized Marathon diabase dykes north of Lake Superior (Buchan et al., 1996), the northwest-trending 2076 +5/-4 Ma Fort Frances swarm west of Lake Superior (Fahrig et al., 1986; Buchan et al., 1996), the 1998 ± 2 Ma Minto swarm of the Ungava Peninsula (Buchan et al., 1998), and possibly the undated, reversely magnetized Marathon dykes (Buchan et al., 1996). Therefore, the paleomagnetic results suggest that most north- to northwest-trending dykes are likely ca. 2120–2000 Ma in age, rather than earliest Paleoproterozoic.

Because of the overlap in orientation and general petrographic character among many of the north- to northwest-trending dykes in the Yasinski Lake area, confident separation of these from each other, and from those of neighbouring diabase swarms, is difficult. As discussed above, paleomagnetic direction information is one criterion by which association with one swarm or another may be made. We have sought to improve this resolution through precise U-Pb (baddeleyite) dating of some of these dykes; we report here results from the first of these efforts, on a north-trending Lac Esprit dyke. The age represents the primary crystallization age of the dyke and identifies a newly recognized swarm of unique age previously unknown in the eastern Superior Province. The new dyke age contributes to dyke-swarm correlations in the Superior Craton and also aids in the assessment of models promoting apparent polar wander and continental drift of Laurentia during the Paleoproterozoic, or block rotation since this time.

ANALYTICAL TECHNIQUES

Approximately 50 kg of sample were collected from the coarse-grained interior of a 45 m thick north-trending dyke along the north shore of Ekomiak Lake (Fig. 2); this dyke carries a typical Lac Esprit paleomagnetic direction. The sample was crushed and finely ground using standard techniques, and then introduced as a wet slurry, slowly, over a shaking (Wilfley) table to concentrate the heavy minerals. This was followed by passage of the concentrate through heavy liquids (methylene iodide, D=3.33), stirring occasionally to ensure the release of attached air bubbles or any adhering lower density phases (*see also* Heaman and LeCheminant, 1993). Isolation of the least-magnetic populations of grains was achieved through the use of a conventional Frantz™ isodynamic magnetic separator up to a current of 1.6A and a side slope of 0°. The best-quality grains of baddeleyite were then handpicked under ethanol using a binocular microscope. All fractions were treated in an ultrasonic bath in ethanol for 30 s in order to remove any affixed phases that might contribute higher levels of common Pb (e.g. feldspar, apatite).

Isotope dilution U-Pb analytical work broadly followed the sample preparation and laboratory methods described by Hamilton et al. (1998) and Parrish et al. (1987). Data have been reduced and analytical errors propagated following the methods of Roddick (1987). Concordia ellipse errors are

Figure 2. *Detail of the Yasinski Lake area, showing the location of the sample site. Dykes* modified after *Goutier and Doucet (1997a, b) and Goutier et al. (1997a, b, c).*

shown at the 2σ (95% confidence) level of uncertainty. Total analytical blanks for Pb and U during this study were <5 pg and <0.5 pg, respectively. Age calculations were carried out using the decay constants 1.55125×10^{-10} year^{-1} for ^{238}U and 9.8485×10^{-10} year^{-1} for ^{235}U (Jaffey et al., 1971).

RESULTS

As illustrated in Figure 3, sample JG97-EKN yielded abundant honey-brown, euhedral, thin, striated blades typical of baddeleyite morphology (c.f. Heaman and LeCheminant, 1993). Five multigrain fractions were prepared, comprising between 4 and 40 grains each.

Least paramagnetic fractions Bd-1 and Bd-2 (Table 1) comprise simple, small populations of short, broken fragments of slightly pale brown, clear baddeleyite. These grains have very low U concentrations (~20–30 ppm); consequently, the amount of radiogenic Pb analyzed for these aliquots is low (30–50 pg) and the associated analytical errors are large. Fractions Bd-3 to Bd-5 consist of larger, less broken grains (up to ~ 40 x 150 µm; Fig. 3a, b) recovered from the slightly more magnetic populations, and have greater U contents (up to 125 ppm) and resultingly increased analytical precision. Calculated Th/U ratios are mostly ~0.08–0.10, somewhat typical for many baddeleyites. Most of the analyses tend to fall slightly below concordia, with fractions Bd-1 to Bd-4 being 1.1–2.0% discordant (Fig. 4). A fifth fraction (Bd-5) was given very light air abrasion treatment for 1.5 hours

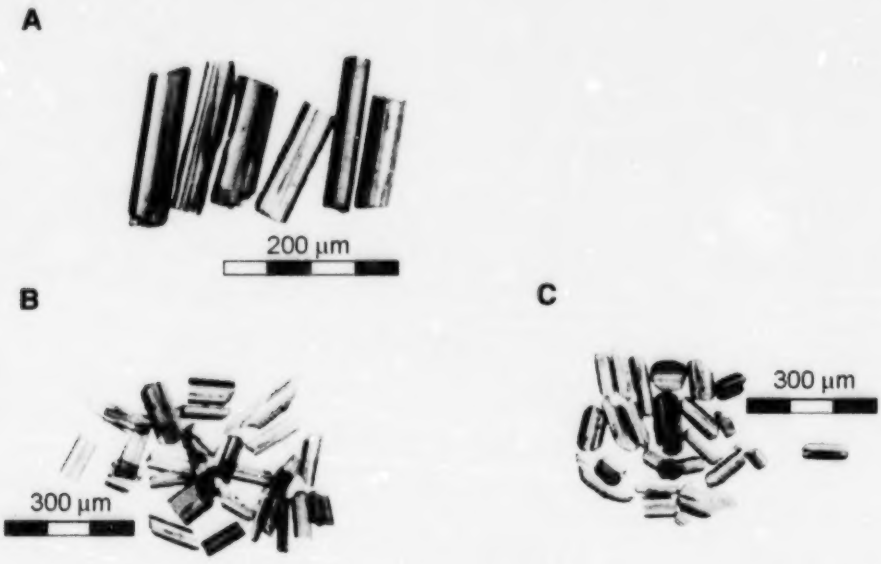

Figure 3. *Representative photomicrographs of baddeleyite grains recovered from coarse-grained interior of Lac Esprit diabase dyke.* ***A****) Euhedral, elongate, striated blades, fraction Bd-3.* ***B****) Broken elongate, striated blades of fraction Bd-5, before abrasion.* ***C****) Fraction Bd-5, following 1.5 hours of light air abrasion.*

Table 1. U-Pb analytical data.

Fraction				Concentrations				Atomic ratios						
Description [1]		# of grains	Wt. µg [2]	U ppm [2]	Pb* ppm [2]	Pb pg [3]	Th/U [4]	$^{206}Pb/^{204}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{238}U$	$^{207}Pb/^{235}U$	$^{207}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$ Age (Ma)	Disc. %
Lac Esprit N-S diabase (z5107; JG97-EKN) Coarse-grained to pegmatitic gabbro (Zone 18, E 332919, N 5917356)														
Bd-1	nm0°, sf	28	4	31	12	8	0.147	437	0.0423	0.3711 ± 0.26%	6.547 ± 0.31%	0.12793 ± 0.23%	2069.7 ± 8.2	2.0
Bd-2	nm0°, sf	20	4	21	8	11	0.091	193	0.0260	0.3743 ± 0.55%	6.599 ± 0.67%	0.12786 ± 0.50%	2068.8 ± 17.6	1.1
Bd-3	m0°, lb	4	3	116	43	2	0.100	3641	0.0288	0.3738 ± 0.10%	6.588 ± 0.11%	0.12784 ± 0.04%	2068.5 ± 1.5	1.2
Bd-4	m0°, lb	40	16	68	25	7	0.078	3365	0.0225	0.3741 ± 0.09%	6.594 ± 0.10%	0.12783 ± 0.04%	2068.3 ± 1.3	1.1
Bd-5	m0°, lb, abr 1.5 hrs	25	9	125	47	13	0.091	1775	0.0261	0.3754 ± 0.09%	6.618 ± 0.11%	0.12785 ± 0.05%	2068.7 ± 1.8	0.8

Errors are 1 σ of mean in % except 207/206 age errors which are 2 σ in Ma; * = Radiogenic Pb

[1] Mineral prefix: Bd = baddeleyite, abr = abraded. Shape: sf = short fragments; lb = long blades
Magnetic properties: nm0° = nonmagnetic at 0 degrees side slope on Frantz™ magnetic separator at maximum current; m0 = magnetic at 0 degrees side slope.

[2] Uncertainties in concentrations are estimated to be <10% for sample weights >10µg, >10% for sample weights <10µg. Uncertainties in sample weights estimated at ± 1µg.

[3] Total common Pb in analysis, corrected for spike and fractionation.

[4] Th/U from 208*/206* and 207*/206* age.

Disc % = Percent discordance on discordia to origin.

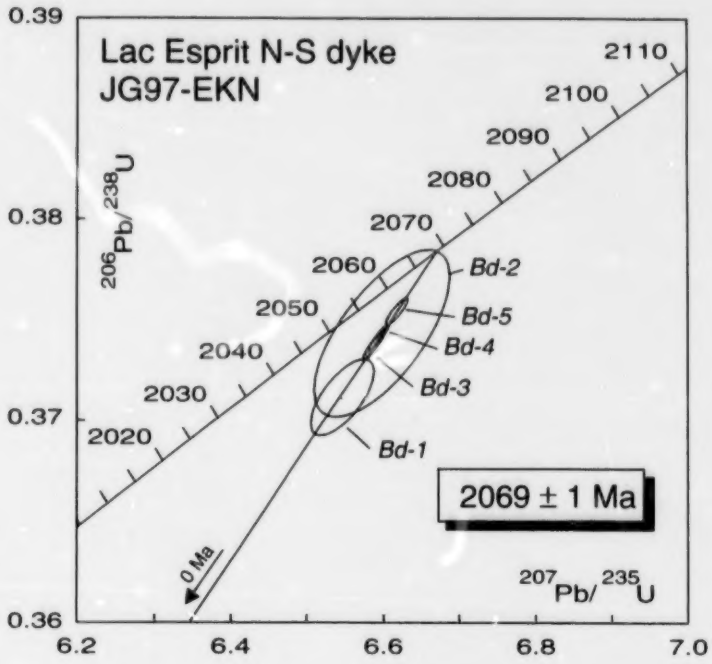

Figure 4.

Uranium-lead concordia diagram for Lac Esprit diabase dyke baddeleyites.

(Fig. 3b, 3c) and is least discordant of all of the analyses, at 0.8% (Table 1), suggesting that, as for zircon, surface-correlated Pb-loss is responsible for at least some of the discordance. Although the platy and delicate nature of most baddeleyite crystals normally precludes the use of air abrasion as a routine method for improving concordance for this mineral, the results reported here suggest that gentle abrasion of one or two coarse fractions may be sufficient to help define a more robust upper intercept, provided enough material is available.

Data for all analyzed baddeleyite fractions in the Lac Esprit dyke are collinear, and, in part, overlapping (Fig. 4). All five analyses have $^{207}Pb/^{206}Pb$ model ages ranging from 2068.3 to 2069.7 Ma. Linear regression of the data, using a modified York (1969) method, results in a poorly constrained lower intercept that is near zero (present day) with large uncertainties. The analyses were thus regressed by forcing the fit through the data and the origin, with a resulting upper intercept age of 2069 ± 1 Ma, having a mean square of weighted deviates (MSWD) of 0.05. This age is interpreted to represent the timing of emplacement and magmatic crystallization of the dyke.

DISCUSSION

The 2069 ± 1 Ma age for the Lac Esprit dyke confirms the conclusion of Ernst et al. (1998), based on paleomagnetism, that many of the extensive north- to northwest-trending dykes east of James Bay belong to a previously unrecognized Paleoproterozoic dyke swarm. The age of the emplacement of the Lac Esprit swarm is considerably younger than that of the ca. 2475 Ma Mistassini or 2473–2446 Ma Matachewan swarms, which possibly extend into the eastern James Bay region with similar trends (Ernst et al., 1996). Indeed, other dykes of this age are not known to occur elsewhere in the eastern Superior Province.

Of other significant Paleoproterozoic dyke swarms in the Superior Province, the fanning and reversely magnetized 2076 +5/-4 Ma Fort Frances swarm (Buchan et al., 1996) compares closely with the age of the reverse Lac Esprit dyke reported here (Fig. 1). Although the geographically intervening north-trending Marathon dykes north of Lake Superior appear to be significantly older at 2121 +14/-7 Ma, Buchan et al. (1996) noted that the subset of undated, but reversely magnetized, Marathon dykes could correlate with the Fort Frances swarm, a hypothesis strengthened by paleomagnetic and geochemical arguments. Recognition that the Lac Esprit dykes represent a major mafic magmatic swarm east of James Bay thus broadens the known extent of ca. 2.07 Ga dyke swarms eastward across approximately two-thirds of the Superior Province. We also note that a suite of east-northeast- and northeast-trending gabbroic dykes occurring adjacent to the northwestern margin of the Superior Province have recently yielded emplacement ages of 2091 ± 2 Ma and 2072 +4/-3 Ma (Fig. 1; Cauchon Lake and Birthday Rapids dykes, respectively; Heaman and Corkery, 1996; Halls and Heaman, 2000). Whereas Halls and Heaman (1997, 2000) have appealed to a model of Superior–Hearne Province rift separation for the origin of these gabbro bodies, Buchan et al. (1996) argued that the age-equivalent (Fort Frances–Marathon reverse) dyke swarms constitute part of a plume-driven giant radiating swarm with a focus located south of Lake Superior. Further U-Pb geochronological investigations, in tandem with paleomagnetic studies, are in progress on other

representatives of the Lac Esprit swarm in order to help understand the relationship of these dykes to Paleoproterozoic mafic magmatism elsewhere in the Superior Province.

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REFERENCES

Buchan, K.L., Halls, H.C., and Mortensen, J.K.
1996: Paleomagnetism, U-Pb geochronology of Marathon dykes, Superior Province, and comparison with the Fort Frances swarm; Canadian Journal of Earth Sciences, v. 33, p. 1583-1595.

Buchan, K.L., Mortensen, J.K., Card, K.D., and Percival, J.A.
1998: Paleomagnetism and U-Pb geochronology of diabase dyke swarms of Minto block, Superior Province, Quebec, Canada; Canadian Journal of Earth Sciences, v. 35, p. 1054–1069.

Ernst, R.E., Buchan, K.L., Goutier, J., Leclair, A., and Lamothe, D.
1998: Reconnaissance paleomagnetic study of diabase dykes of James Bay and Ashuanipi regions of Quebec; *in* Program and Abstracts; Geological Association of Canada–Mineralogical Association of Canada, Annual Meeting, p. A53.

Ernst, R.E., Buchan, K.L., West, T.D., and Palmer, H.C.
1996: Diabase (dolerite) dyke swarms of the world: first edition; Geological Survey of Canada, Open File 3241, 104 p.

Fahrig, W.F., Christie, K.W., Chown, E.H., Janes, D., and Machado, N.
1986: The tectonic significance of some basic dyke swarms in the Canadian Superior Province with special reference to the geochemistry and paleomagnetism of the Mistassini swarm, Quebec, Canada; Canadian Journal of Earth Sciences, v. 23, p. 238–253.

Goutier, J. and Doucet, P.
1997a: Lac Esprit (33 F/05), Ministère des Ressources naturelles, Quebec, carte SI-33F05-C3G-97K, scale 1:50 000.
1997b: Lac Kowskatchkakmow (33 F/06), Ministère des Ressources naturelles, Quebec, carte SI-33F06-C36-97K, scale 1:50 000.

Goutier, J., Beausoleil, C., Chalifour, S.
1997a: Lac Vion (33 F/12), Ministère des Ressources naturelles, Quebec, carte SI-33F12-C3G-97K, scale 1:50 000.

Goutier, J., Beausoleil, C., Chalifour, S. (cont.)
1997b: Passe Chimusuminu (33 F/11), Ministère des Ressources naturelles, Quebec, carte SI-33F11-C36-97K, scale 1:50 000.
1998a: Lac Langelier (33 F/03), Ministère des Ressources naturelles, Quebec, carte SI-33F12-C3G-97K, scale 1:50 000.

Goutier, J., Dion, C., Lafrance, I., David, J., Parent, M., and Dion, D.-J.
1997c: Lac Threefold (33 F/04), Ministère des Ressources naturelles, Quebec, carte SI-33F04-C3G-97K, scale 1:50 000.
1999: Géologie de la région des lacs Langelier et Threefold (SNRC 33 F/03 et 33 F/04); Ministère des Ressources naturelles du Quebec, RG 98-18, 52 p.

Goutier, J., Doucet, P., Dion, C., Beausoleil, C., David, J., Parent, M., and Dion, D.-J.
1998b: Géologie de la région du lac Kowskatchkakmow (SNRC 33 F/06); Ministère des Ressources naturelles du Quebec, RG 98-16, 48 p.

Halls, H.C. and Heaman, L.M.
1997: New constraints on the Paleoproterozoic segment of the Superior Province apparent polar wander path from U-Pb dating of Molson dykes, Manitoba; *in* Program and Abstracts; Geological Association of Canada–Mineralogical Association of Canada, Annual Meeting, p. A61.
2000: The paleomagnetic significance of new U-Pb age data from the Molson dyke swarm, Cauchon Lake area, Manitoba; Canadian Journal of Earth Sciences, v. 37, p. 957–966.

Hamilton, M.A., Ryan, A.B., Emslie, R.F., and Ermanovics, I.F.
1998: Identification of Paleoproterozoic anorthositic and monzonitic rocks in the vicinity of the Mesoproterozoic Nain Plutonic Suite, Labrador: U-Pb evidence; In Radiogenic Age and Isotopic Studies: Report 11; 1998-F, p. 23–40.

Heaman, L.M.
1997: Global mafic magmatism at 2.45 Ga: remnants of an ancient large igneous province?; Geology, v. 25, p. 299–302.

Heaman, L.M. and Corkery, T.
1996: U-Pb geochronology of the Split Lake Block, Manitoba: preliminary results; *in* Trans-Hudson Orogen Transect, (ed.) Z. Hajnal and J. Lewry; Lithoprobe Report 55, p.60–67.

Heaman, L.M. and LeCheminant, A.N.
1993: Paragenesis and U–Pb systematics of baddeleyite (ZrO_2); Chemical Geology, v. 110, p. 95–126.

Jaffey, A.H., Flynn, K.F., Glendenin, L.E., Bentley, W.C., and Essling, A.M.
1971: Precision measurements of half lives and specific activities of ^{235}U and ^{238}U; Physics Reviews, v. C4, p. 1889–1906.

Mortensen, J.K. and Ciesielski, A.
1987: U-Pb zircon and sphene geochronology of Archean plutonic and orthogneissic rocks of the James Bay region and Bienville Domain, Quebec; *in* Radiogenic Age and Isotopic Studies: Report 1; Geological Survey of Canada, Paper 87-2, p. 129–134.

Parrish, R.R., Roddick, J.C., Loveridge, W.D., and Sullivan, R.W.
1987: Uranium-lead analytical techniques at the geochronology laboratory, Geological Survey of Canada; *in* Radiogenic Age and Isotopic Studies: Report 1; Geological Survey of Canada, Paper 87-2, p. 3–7.

Roddick, J.C.
1987: Generalized numerical error analysis with applications to geochronology and thermodynamics; Geochimica et Cosmochimica Acta, v. 51, p. 2129–2135.

York, D.
1969: Least-squares fitting of a straight line with correlated errors; Earth and Planetary Science Letters, v. 5, p. 320–324.